Applications of Lignophenol / Nano-Structured Titanium Dioxides Composites

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Lignophenols, which are recyclable phenolic lignin-based polymers, have been directly synthesized from lignocellulosics through the phase-separation system composed of surface reactions between concentrated acids and phenols under mild conditions. Lignophenols and their derivatives easily produced particular composites with nano-structured titanium dioxides, having vivid yellow appearances when mixing under heterogeneous conditions. Lignophenols saturated on titanium dioxides within 100 sec. in acetone solutions. As the composites were stable under both aqueous and organic phases except an alkaline condition, lignophenols were easily collected and recovered from various homogeneous conditions. The composites showed charge separations by light irradiation in photochemical cells. These composites also have heat resistance over 300 °C under N_2 atmosphere. These results implied that titanium dioxides were spread over lignophenol molecules. The composites are expected as new recyclable and sustainable materials based on forest carbon resources.
Key words: lignin, lignophenol, titanium dioxide, nano material, composite

1. INTRODUCTION

Recently biomass has been attracted as a substitution for fossil carbon resources because of its sustainability in bio-system on the earth. Lignocellulosics such as wood or grasses have been widely utilized as constructions, fuels and paper pulping. In order to utilize lignocellulosics efficiently, it is necessary to separate main components, cellulose, hemicellulose and lignin without damages. But it was difficult to separate lignin with keeping the properties because native lignin has high sensitivity for change of circumstances. In 1988, novel separation method for lignocellulosics under mild condition has been developed by Funaoka *et al* [1]. Through the phase-separation system composed of a concentrated acid and phenol, lignocellulosics are easily converted to carbohydtares and phenolic lignin-based polymers (lignophenols) under 1 atm at room temperature (Fig.1) [1-3].

Lignophenols has 1,1-bis(aryl)propane-2-*O*-arylether type structures. This structure has high electron density,
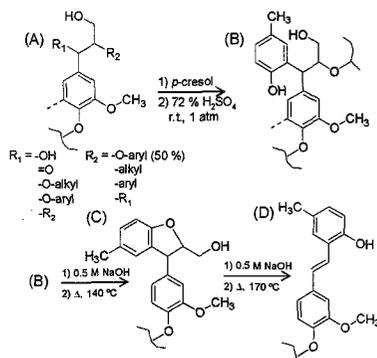

Fig.1. Synthesis of lignophenol and its derivatives directly from lignocellulosics. (A) Softwood native lignin in lignocellulosics, (B) lignophenols (*p*-cresol type), (C) second derivative-I after neighboring group participation (phenol switching) and (D) second derivative-II after aryl migration.

switching functionality and expansion for modification such as hydroxyl groups or *ortho*-positions of phenols. By switching functionality, both arylcoumaran type structures (second derivative-I, Fig.1C) and stylbene type structures (second derivative-II, Fig.1D) were formed by neighboring group participation and aryl migration under alkaline conditions, respectively (Fig.1) [4,5].

Titanium dioxide (TiO_2) is well-known as a white additive for foods, plastics and medicals. Especially, anatase crystal of TiO_2 acts as photocatalysis under UV irradiation or nano-porous electrodes for photochemical cell. Recently a nano-porous electrode of TiO_2 sensitized by lignophenols has been investigated [6-10]. In the preparation process particular adsorption of lignophenol onto TiO_2 was discovered. In this study, applications of the interaction between lignophenols and TiO_2 were carried out.

2. EXPERIMENTAL

2.1 Synthesis of lignophenols

Hinoki cypress (*Chamaecyparis obtusa*) was used as a softwood material. The woody material was milled for 80 mesh passed. Extractives in the material were removed by acetone at room temperature for 72 hrs. A lignophenol has been synthesized following the phase-separation system [3-5]. "Two-step method (process II)", which contains refinery process by immersing into excess water, was carried out as following in the literatures [4-5]. The material (500 g) was added into acetone solution of *p*-cresol (0.5 molL^{-1}). The concentration of this solution corresponds to 3 mol / phenylpropane units (C_9 units), which were subunits of native lignin calculated by Klason method. After evaporation of acetone, a 72 % H_2SO_4 aq. solution was immersed into the material absorbed *p*-cresol at 30 °C. Then the mixture was stirred vigorously soon after immersing H_2SO_4. After 60 min, the mixtures were

soaked into 20 L of de-ionized water with vigorously stirring by a homogenizer for 5 min. Then purple precipitates were washed until pH become 5. After drying the precipitates lignophenol was extracted by acetone. The lignophenol in acetone was refined by dropping into diethylether (EtOEt) under vigorously stirring in chilled condition. After evaporating and drying on P_2O_5, Hinoki cypress-lignophenol (p-cresol type, HCLC) was obtained (Fig.1B).

2.2 Synthesis of second derivatives

HCLC (1.0 g) was dissolved into 80 mL of 1.0 M NaOH. The HCLC solution was poured into a SUS autoclave (100 mL). The autoclave was heated at 120, 140 and 170 °C for an hour. After cooling, the reaction mixture was adjusted to pH 2 by 2.0 M HCl. Resulting precipitates were washed by water. After drying on P_2O_5, Second derivatives of HCLC (HCLC120, HCLC140 and HCLC170) were obtained (Fig.1C, D).

2.3 Characterization of lignophenols

The structure of HCLC was characterized by Gel Permeation Chromatography (GPC), ^1H-NMR and Thermal Mechanical Analysis (TMA). GPC was carried out by LC-10 system (Shimadzu Co.) with four columns (KF801, KF802, KF803 and KF804, Shodex Co.), using tetrahydrofuran (THF) after distillation as an eluent. M_w and M_n were determined based on standard polystyrene. ^1H-NMR spectrum was measured by JNM-A500 (JOEL Co.) in $CDCl_3$ or $CDCl_3$ / C_5D_5N = 3 / 1 (v / v). TMA was also carried out by TMA-SS (SII Inc.) in the temperature range 50-280 °C at a rate of increase of 2 °Cmin^{-1}, using penetrating technique for a measurement. UV-Vis spectroscopy was carried out on a UV-560 (JASCO Co.). FT-IR spectroscopy was also carried out on a Spectrum GX (Perkin Elmer Co.), using the KBr pellet technique for sample preparation.

2.4 Preparation of LP / TiO_2 composites

HCLC composites were prepared with both TiO_2 (ST01, Ishihara Sangyo Co.) and TiO_2 thin films. The TiO_2 thin films were prepared on a fluorine-doped tin oxide coating glasses (FTO glasses) by sintering at 450 °C under aerobic condition [6-9]. TiO_2 were dried under 110 °C for 24 hrs before preparation. HCLC / TiO_2 composites (LP/TiO_2) have been prepared by immersing TiO_2 into HCLC and its derivatives solutions at room temperature. Resulting yellow precipitates were evaporated and dried over P_2O_5 under dark conditions. Nano-structured TiO_2 of the thin films also produced composites with HCLC in the same ways[10]. The dry precipitates were analyzed by TMA, FT-IR and diffuse and reflection UV-vis spectroscopy.

2.5 Extraction of HCLC

Extraction of HCLC and its derivatives from LP/TiO_2 was carried out by a 1.0 M NaOH solution under dark condition with a stirring system. Amounts of lignophenols were estimated by UV-Vis spectroscopy. Characteristics of extracted lignophenol were determined by ^1H-NMR, FT-IR and TMA after neutralized by 1.0 M HCl for pH = 2.0.

2.5 Photo-electricity conversion

Performance of LP/TiO_2 as a photo-electricity conversion under visible light irradiation was composed of a composition, FTO-TiO_2-LP-Electrolyte-Pt-FTO. The electrolyte was 0.5 M LiI, 0.05 M I_2 in acetonitrile. Photovoltaic performance was measured by Potentiostat (HA-105, Hokuto Denko Co.) under 150-W Xe lamp irradiation through a L41 UV-cut filter.

3. RESULTS AND DISCUSSION

3.1 Lignophenol/TiO_2 composites

Lignophenol/nano-structured TiO_2 composites were easily produced under every condition except an alkaline condition. Stable composites have been produced only by mixing under heterogeneous conditions. The resulting composites have yellow appearances. Not only lignophenol polymers, but derivatives of lignophenol
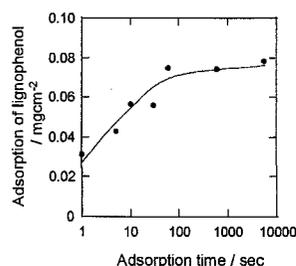

Fig.2. A time-course for adsorption of second derivative-I of Hinoki cypress-lignophenol (p-cresol type, HCLC140) on a nano-porous TiO_2 electrode. HCLC140 was extracted by 0.5 M NaOH. Evaluation was carried out by UV-Vis spectroscopy at λ = 320 nm.

behaved in the same ways.

The equilibrium was accomplished within 100 sec at room temperature. For example, Fig.2 illustrates the time course for adsorption of second derivative-I of HCLC (HCLC140, Fig.1C) in acetone solution. This tendency was observed by all lignophenols and derivatives[8]. Since acetone has high affinity for lignophenols and their derivatives, entropy of this phase rapidly increased. But this adsorption naturally proceeding, therefore there is probably a large enthalpy gain (Fig.3A). Since the equilibrium was largely shifted to the composites, lignophenol was not extracted by acetone. This stability can be utilized to selective heterogeneous separation of lignophenol from various solutions.

Although this composite was stable in various solvents, lignophenols were easily extracted by alkaline media such as NaOH solution. Under this condition the equilibrium was inclined to separation in contrast. Since lignophenols showed distinguished absorbance under
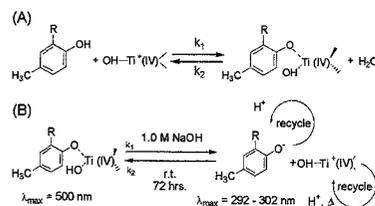

Fig.3 Schematic model for proposed mechanism: (A) adsorption of lignophenol on TiO_2 with esterification and (B) extraction by 1.0 M NaOH.

this condition at a wavelength range λ = 292-302 nm based on π–π* transition of phenolate ions (Fig.3B). Lignophenols were recovered from the phenolate ions by neutralization with acid. As lignophenols are separated, TiO₂ is recycled at the same time. In fact, TiO₂ acted as an absorber for lignophenols in the second use with 70 % of ability. In the repeated uses, this performance was kept after 5 times recycling. Therefore this process would utilize as collection technique.

As the interactions between phenols and TiO₂ have been investigated in the previous literatures [11-18], both chelation and esterification would be occurred. Because of easy extraction by NaOH and hard separation by acetone, ester type linkages mainly exist on the surface of TiO₂. Probably these linkages are stronger than hydrogen bonding of aliphatic hydroxyl groups on C₃ position in C₉ units. Moreover, red shifts of absorption spectra implied that charge transfer (CT) complexes were produced. Therefore 1,1-bis(aryl)propane units approached the TiO₂, because these linkages were produced at phenolic hydroxyl groups.
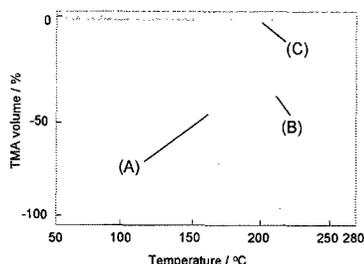

Fig.4 Profiles for thermal mechanical analysis (TMA) of (A) Hinoki cypress-lignophenol (*p*-cresol type, HCLC), (B) bulk mixture of HCLC/ST01=33/67(w/w) and (C)HCLC/ST01 nano composite. TMA was carried out under 150 mLmin⁻¹ of N₂ flow using penetration technique in the temperature range 50-280 °C at a rate of 2 °Cmin⁻¹.

Fig.4 showed thermal plasticity of (A) HCLC and (C) HCLC/TiO₂ composites estimated by TMA. Although HCLC showed thermal plasticity at a range of 158-170 °C, HCLC/ST01 has never plasticized. In contrast, bulk mixture showed partial plasticity up to 40 % at 165-250 °C (Fig.4B). Therefore TiO₂ was well dispersed in lignophenol molecules with interactions. These results indicated TiO₂ was well dispersed between molecular chains with interaction occurred at each 1,1-bis(aryl)propane unit.
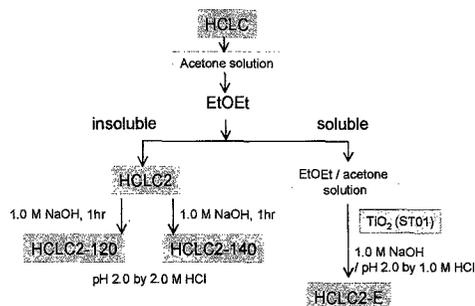
3.2 Applications

Fig.5 A flow chart for refinery for Hinoki cypress-lignophenol (*p*-cresol type, HCLC) with diethyl ether (EtOEt). Ether soluble moiety was collected by ST01. Second derivatives of HCLC were synthesized from HCLC2.

These affinities of lignophenols to TiO₂ were utilized for following two applications.

3.2.1 Improvement of lignophenol synthesis process

An improvement for synthesis process of lignophenol was carried out with TiO₂. In the present industrial production of lignophenol, two-step method / process-II was used for both the system plants No.1 (Tsu city, Mie university, JST CREST) and No.2 (Kitakyushu city, Forestry Agency). In this process, acid/phenol reaction mixtures were immersed into excess de-ionized water under stirring to separate carbohydrates and to remove acids after phase-separation reaction. Although most of lignophenol aggregated under the acidic condition, a part of lignophenol is dispersed or dissolved.

In order to remove HCLC, nano-sized TiO₂ powder (ST01) was immersed into an acidic carbohydrate solution (Fig.6B) with pH = 3 after dilution by 20-L of water for 5 times. Soon after ST01 immersing, yellow precipitates were obtained. At the same time, beige suspension gradually became clear. After centrifugation (3 500 rpm), precipitates were separated from top clear perfectly. Beige HCLC dispersing in the solution was turned into yellow composites with ST01. Interestingly, pH of the solution increased to 7. Because ST01 have a lot of Ti-OH structures on the surfaces as shown in FT-IR spectrum (3400 cm⁻¹), H⁺ was adsorbed. Consequently, two merits were obtained by ST01, removal of lignophenol and increase of pH. Though over 200 L of water was needed in conventional way, only less than 100 L was sufficient for neutralization with ST01. Moreover *p*-cresol remained in acidic solution was removed by ST01. Therefore this TiO₂ technique improved water consumption, working time and phenol removal.

The precipitates were separated to HCLC and ST01 perfectly by extracting in NaOH solutions. Though the amounts of lignophenols adsorbed on the recycled ST01 decreased to 70 % compared to the first adsorption, the performance was kept to the fifth trial.

Generally, the purification of resulting lignophenol from remained phenol was carried out by aggregation of insoluble moieties in a poor solvent such as EtOEt. Although a part of lignophenol was dissolved into EtOEt,
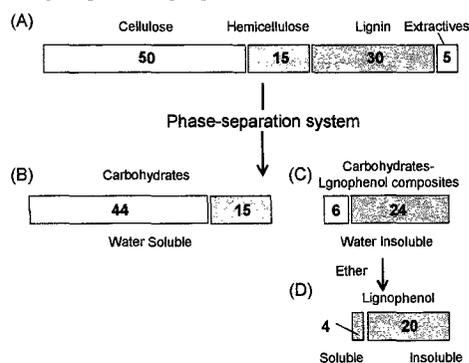

Fig.6 The material balance for synthesis of Hinoki cypress - lignophenol (*p*-cresol type) through the phase-separation system (two-step method, process-II) in the system plant (No.1, Mie university). Acidic media was 72 % H₂SO₄. Reaction was carried out under N₂ at 30 °C for 60 min. (A) Composition for Hinoki cypress, (B) water soluble moieties, (C) water insoluble moieties and (D) both diethyl ether soluble and insoluble fractions after acetone extraction.

it is difficult to collect ether soluble moieties because high flammability, high volatile and explosive peroxides (Fig.6D). Then collections of these ether-soluble moieties by ST01 were tried under dark condition in order to prevent from photocatalytic reactions of ST01 (Fig.5). Soon after immersing ST01, vivid yellow lignophenol/ST01 composites were also produced. The composites were precipitated naturally within 10 min. The ether-soluble moieties were collected for 75-80 % yield. Both the lignophenol and ST01 were recycled in the same way in the collection under acidic conditions. Consequently, the yield of lignophenol was improved from 20 % to 22.5 % based on lignocellulosics, with 12.5 % increase for lignophenol.

As properties of HCLC2 and HCLC2-E were compared, differences were observed obviously in size of molecules. Average molecular weights of HCLC2 and HCLC2-E were M_w = 14 676, M_w / M_n = 4.09 and M_w = 1 586, M_w / M_n = 1.81, respectively. The molecular size of HCLC2-E was smaller than that of second derivative-I of HCLC2 (HCLC2-140, M_w = 2 329, M_w / M_n = 2.22). Though HCLC2-140 was synthesized by switching functionality which is particular recycling and down-sizing technique of lignophenol [4-5], smaller fractions than HCLC2-140 were easily obtained from EtOEt solutions. Moreover, the amount of grafting phenol of HCLC2-E (0.89 mol/C_9) was larger than that of HCLC2 (0.82 mol/C_9) for 10 % estimated by ^{1}H-NMR. This result was also confirmed by FT-IR spectra (Fig.7). Especially, absorbance of 813-815 cm^{-1} corresponded to vibration of neighboring 2H out of plane for *p*-cresol obviously increased. On the other hand, other peaks showed same structures in HCLC2 and HCLC2-E. These results implied 1,1-bis(aryl)propane type structures increase in the molecules of HCLC2-E. Since increase of this structure will contribute improvement of electron density, various new properties are expected. Therefore this separation method was applied to selective extraction of small molecules.
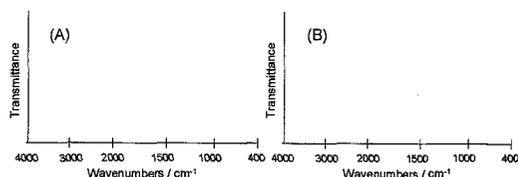

Fig.7 FT-IR spectra for lignophenols. (A) EtOEt insoluble moieties of Hinoki cypress-lignophenol (*p*-cresol type, HCLC2) and (B) HCLC-2E recycled by ST01.

3.2.2 Photo-electricity conversion

As described in our previous literatures [6-10], photo-sensitization of lignophenol and its derivatives for nano-porous TiO$_2$ were realized under visible light irradiation. Lignophenols with both small molecules and high electron densities will act as good photosensitizers. In fact, the amounts of HCLC413 adsorbed on TiO$_2$ were twice larger than HCLC. The best performance of photo-electricity conversion was V_{oc} = 0.51 V, I_{sc} = 10.23 mAcm^{-2}, FF = 0.59 and η = 3.61 % under visible light irradiation [9]. Moreover, ether soluble fractions (HCLC2-E) also showed same tendency. The HCLC2-E showed larger performance of η = 0.52 % than HCLC2
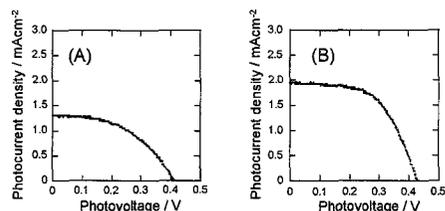

Fig.8 Photovoltaic performances of photochemical cell sensitized with lignophneols under 150-W Xe lamp irradiation through L41 UV-cut filter. (A) Hinoki cypress –lignophenol (*p*-cresol type, HCLC2) and (B) HCLC2-E.

(η = 0.28 %) (Fig.8). These charge-separations under irradiation will be improved by adsorption frequency and electron density of lignophenols.

4. CONCLUSIONS

HCLC and its derivatives produced stable composites with nano-structured TiO$_2$. The composites were applied in two ways. First, improvement of refinery process in both aqueous and organic solutions was carried out. Second, photo-electricity conversion devices under visible light were prepared. Lignophenol / TiO$_2$ composites are probably expected to be applied in various scenes.

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